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(54) THERMALLY DEVELOPABLE PHOTSENSITIVE MATERIAL FOR X-RAY  
PHOTOGRAPHS

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## (54) THERMALLY DEVELOPABLE PHOTSENSITIVE MATERIAL FOR X-RAY PHOTOGRAPHS

### CLAIMS

Thermally developable photosensitive material characterized by consisting of one or more layers of thermally developable photosensitive elements consisting of (a) oxidation-reduction image-forming component from a reducible organic silver salt and reducing agent, (b) photosensitive silver halide and(or) photosensitive silver halide-forming component and (c) binder on a support, with the thermally developable photosensitive element containing (d) at least one component emitting light that is effective for sensitizing the photosensitive silver halide by X-ray irradiation, in the same layer and(or) neighboring layer.

### DETAILED EXPLANATION OF THE INVENTION

#### INDUSTRIAL APPLICATION FIELD

The present invention deals with the development of thermally developable photosensitive materials for X-ray photographs, which have sufficient X-ray photographing sensitivity and give high-resolution images upon thermal development.

#### CONVENTIONAL TECHNOLOGY

There have been many photosensitive materials for X-ray photographs. The usual silver salt photosensitive materials have been widely used for non-destructive tests for semiconductor products, electronic parts, printed circuit boards, various composite materials, metal parts, sintered products, etc. However, conventional X-ray photographic photosensitive materials have to be developed under wet conditions with poor workability and complex management of developer solutions.

Dry processing thermally developable photosensitive materials, typically shown in Japanese Kokoku Patent No. SHO 43[1968]-4924 have low sensitivity to X-rays and are not suitable for direct X-ray photography. When photographed using a fluorescent sensitization paper to supplement the poor sensitivity, the sharpness decreases greatly, and is not suitable for applications requiring high resolution.

## OBJECTIVE OF THE INVENTION

The objective of the present invention is to develop X-ray photographic photosensitive materials that can be thermally developed by a simple dry process and that have excellent resolution.

## CONSTITUTION OF THE INVENTION

The objective of the present invention can be achieved by creating a thermally developable photosensitive material characterized by having one or more layers of thermally developable photosensitive elements consisting of (a) oxidation-reduction image-forming component from a reducible organic silver salt and reducing agent, (b) photosensitive silver halide and/(or) photosensitive silver halide-forming component and (c) binder on a support; the thermally developable photosensitive element contains (d) at least one component emitting light that is effective for sensitizing the photosensitive silver halide by X-ray irradiation, in the same layer and(or) neighboring layer.

The components that emit light upon X-ray irradiation, used in the present invention, may be phosphors used in the usual X-ray sensitizing papers, etc. Specific examples of preferred phosphors are shown below:

- (1) ZnS : Ag
- (2) ZnS : Cu, Al
- (3) (Zn, Cd) S : Cu, Al
- (4) ZnS : Au, Al
- (5) ZnS : Cu
- (6) (Zn, Cd) S : Cu
- (7) (Zn, Cd) S : Ag
- (8) CaWO<sub>4</sub>
- (9) Gd<sub>2</sub>O<sub>2</sub>S : Tb
- (10) La<sub>2</sub>O<sub>2</sub>S : Tb
- (11) Y<sub>2</sub>O<sub>2</sub>S : Tb
- (12) BaSO<sub>4</sub> : Pb
- (13) BaFCl : Eu<sup>2+</sup>
- (14) LaOBr : Tb, Tm

In the present invention, when the component emitting light upon X-ray irradiation is included in the same layer of the thermally developable photosensitive element, and if too small an amount is added, then uniform light emission is not obtained,

resulting in poor granularity of the image; furthermore, sufficient X-ray sensitivity is not obtained. On the other hand, when an excess amount is used, the light emission by X-ray irradiation is saturated, surface matting occurs, and a sufficient density cannot be obtained. Also, when it is included in a neighboring layer of the thermally developable photosensitive element, e.g., undercoating layer, in the case when too little is added, then uniform light emission is not obtained, resulting in poor granularity of the image; furthermore, sufficient X-ray sensitivity is not obtained. On the other hand, when an excess amount is used, the light emission by X-ray irradiation is saturated, and X-ray sensitivity is not enhanced.

Therefore, in the present invention, the amount of the component emitting light by X-ray irradiation, added into the same layer as and(or) neighboring layer, should be 0.5-30, preferably 1.5-10 g/m<sup>2</sup>. There are no specific restrictions in the method and timing of addition of the component emitting light by X-ray irradiation.

The thermally developable photosensitive elements used in the present invention consist of (a) oxidation-reduction image-forming component from a long-chain fatty acid silver salt and reducing agent, (b) photosensitive silver halide and(or) photosensitive silver halide-forming component and (c) binder, with all of them in a single layer, while the long-chain fatty acid silver salt and reducing agent may be included in different layers; also, a long-chain fatty acid silver salt or reducing agent may be added to the upper or lower layer of the single layer described above. For preventing dark discoloration, etc. of the long-chain fatty acid silver salt in the component (a) under room light, those containing 12-24 carbon atoms are preferred, more specifically, silver behenate, silver stearate, silver palmitate, silver myristate, silver laurate, silver oleate, silver hydroxystearate, etc., while silver behenate is most effective.

There are many types of reducing agents that can be used in the oxidation-reduction image-forming component. In general, they include commonly used developing agents for silver halide photosensitive materials, more specifically, hydroquinone, methylhydroquinone, chlorohydroquinone, methylhydroxynaphthalene, N,N'-diethyl-p-phenylenediamine, aminophenol, ascorbic acid, 1-phenyl-3-pyrazolidone, etc. and others such as 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 4,4'-butylidenebis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), etc., bisnaphthol-type reducing agents disclosed in Japanese Kokai Patent No. SHO 46[1971]-6074, 4-benzenesulfonamidophenol compounds disclosed in Belgian Patent No. 802519.

Especially for photosensitivity, it is necessary that the thermally developable photosensitive elements contain silver halides such as silver chloride, silver bromide,

silver iodide, silver iodobromide, silver iodochloride, and silver iodochlorobromide. Such silver halides in fine grain form are especially effective. The fine silver halide grains can be prepared by halogenating a portion of the reducible organic silver salt by a silver halide-forming component such as ammonium bromide, lithium bromide, sodium chloride, N-bromosuccinimide, etc. Adding the so-called external silver halide can also be done.

Such thermally developable photosensitive elements containing an external silver halide are disclosed in, e.g., Belgian Patent No. 774436. Namely, first, a photosensitive silver halide prepared separately from the oxidation-reduction image-forming component is mixed with the image-forming component. The preferred silver halide (or silver halide-forming component) content is 0.001-0.3 mol, more preferably 0.01-0.15 mol/mol of reducible organic silver salt.

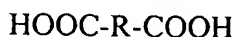
In the present invention, the thermally developable photosensitive elements contain one or more binders in the layer. The binders may be hydrophilic or hydrophobic and transparent or semi-transparent, more specifically, polyvinyl butyral, cellulose acetate butyrate, polymethyl methacrylate, polyvinylpyrrolidone, ethylcellulose, cellulose acetate, polyvinyl acetate, polyvinyl alcohol, gelatin, compounds containing sulfobetaine repeating units as disclosed in Canadian Patent No. 774054, etc. The ratio of binders to the reducible organic silver salt should be 10:1 to 1:10, preferably 4:1 to 1:2 by weight.

In the thermally developable photosensitive elements, it is preferred to use organic acids for improved image tone and post-development stability. Using one or more fatty acids the same as or similar to that in the long-chain fatty acid silver salts is especially preferred. The amount of such fatty acids used should be 25-200 mol%, preferably 30-120 mol%, in relation to the reducible organic silver salts.

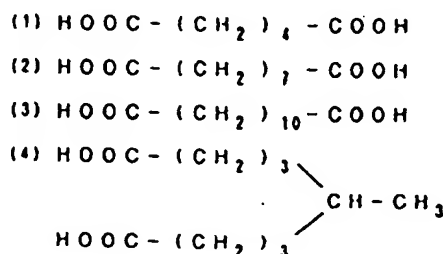
The thermally developable photosensitive elements in the present invention may contain toners, such as phthalazinone and its derivatives described in US Patent No. 3080254; cyclic imides described in Japanese Kokai Patent No. SHO 46[1971]-6074; phthalazinedione compounds described in Japanese Kokai Patent No. SHO 50[1975]-32927, etc.

The thermally developable photosensitive elements in the present invention may also contain antifogging agents such as mercury compounds described in Japanese Kokoku Patent No. SHO 47[1972]-11113; 1,2,4-triazole compounds described in Japanese Kokai Patent No. SHO 55[1980]-42375; tetrazole compounds described in Japanese Kokai Patent No. SHO 57[1982]-30828; benzoic acid derivatives described in Japanese Kokai Patent No. SHO 57[1982]-138630; sulfonyl group-containing compounds described in Japanese Kokai Patent No. SHO 57[1982]-147627; dibasic

acids described in Japanese Kokai Patent No. SHO 58[1983] -107534, etc. Especially in the present invention, dibasic acids described in Japanese Kokai Patent No. SHO 58[1983]-107534 are preferred for antifogging agents. Such dibasic acids can be represented by the general formula given below:



In the formula, R represents an alkylene or alkenylene [-containing] group of 4 or more carbon atoms. Specific examples of such compounds include:



The thermally developable photosensitive elements in the present invention may also contain development promoters, hardeners, antistatic agents (layers), UV absorbers, fluorescent whiteners, filter dyes (layers), etc.

The thermally developable photosensitive elements in the present invention may also contain spectral sensitizers. Effective spectral sensitizers include cyanine dyes, merocyanine dyes, and xanthene dyes, especially those described in Product Licensing Index, Vol. 92, pp.107-110 (December 12, 1971) or Belgian Patent No. 772371.

The thermally developable photosensitive elements in the present invention are formed on an appropriate support to obtain thermally developable photosensitive materials. The supports may be synthetic resin films such as polyethylene, polypropylene, polyethylene terephthalate, polycarbonates, cellulose acetate, etc.; synthetic paper, paper coated with a synthetic resin film such as polyethylene, art paper, photographic baryta paper, metal plates (foils) such as aluminum, etc., metal vapor-deposited synthetic resin films or glass plates, etc.

## Examples

Next, the present invention is explained with examples. However, the present invention is not limited to such examples.

## APPLICATION EXAMPLE 1

According to Japanese Kokai Patent No. SHO 58[1983]-139135, solid silver bromide was prepared as a photosensitive component in a polymer by the method described below.

A dispersion was prepared from 5.9 g of silver stearate and 1000 mL of ethanol in a homomixer, treated with 40 g of polyvinyl butyral, stirred for dissolution, heated to 50°C, treated while stirring with a solution of 23 g of N-bromoacetamide and 12 mg of lithium bromide in 250 mL of acetone over a period of 1 h, cooled to 40°C, and poured into 5000 mL of water. The precipitate was filtered out and dried to obtain 110.3 g of stearic acid-containing solid silver bromide in polyvinyl butyral. The solid silver bromide was used to make a photosensitive solution according to the method described below.

A dispersion was prepared by dispersing 25 g of silver behenate, 20 g of behenic acid and 25 g of Illustration Compound (8) (product of Kasei Optonics Co.; tradename: Kyokukokeikotai [transliteration] P5B1) in a mixture of 300 mL of xylene and 300 mL of n-butanol, treated with 4.4 g of the above solid silver bromide, then with 50 g of polyvinyl butyral and stirred for dissolution. The resulting polymer dispersion of silver behenate containing photosensitive silver halide was treated with 2 g of azelaic acid, 7 g of phthalazinone, 20 g of 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 0.1 g of homophthalic acid, then with 0.003 g of 2-(1'-ethylbenzoxazolidene)rhodanine, to obtain a photosensitive solution, which was then coated, using a roll coater, on a photographic base paper to 13.5 g/m<sup>2</sup> dry.

The coated paper was topped by a polymer layer using a 7% aqueous solution of polyvinyl alcohol (product of Nippon Gosei Kagaku Kogyo Co., tradename: Gohsenol NH-18) to 1.5 g/m<sup>2</sup> dry to obtain sample (A). For comparison sample (B) was prepared similarly as in sample (A) without using the Illustration Compound (8). Sample (C) was prepared similarly as in the sample (A) using 25 g of Illustration Compound (1) (product of Kasei Optonix Co., tradename: Kyokukokeikotai SL) in place of the Illustration Compound (8). Sample (D) was prepared using 0.003 g of 1-carboxymethyl-5-[(3'-ethylnaphtho[1',2'-d]oxazolinon-2'-ylidene)-3-allylthiohydantoin in place of 2-(1'-ethylbenzoxazolidene)rhodanine, and also using Illustration Compound (5) (product of Kasei Optonix Co., tradename: Kyokukokeikotai LCG1A) in place of Illustration Compound (8) of sample (A). Sample (E) was prepared using 25 g of Illustration Compound (9) (product of Kasei Optonix Co., tradename: Kyokukokeikotai P43) in place of the Illustration Compound (5) of sample (D). In sample (A), the amount of Illustration

Compound (8) used was changed to 12.5 g to obtain sample (F) and to 50 g to obtain sample (G).

Using an X-ray source of the soft X-ray non-destructive tester SV-100A of Softex Co., the above samples were irradiated with X-rays at 4 mA x 80 KVP, with the back side of the photosensitive material [in] contact being passed over a hot plate for thermal development for image formation. The thermal development occurred at 120°C for 10 sec. The resulting images were measured for maximum density and fog density. Results obtained are given in Table 1, with S10 being the X-ray dosage to give a density of 1.0 (as a relative value based on 100 for the X-ray dosage of sample (B).) (Application Example 3 is similarly illustrated.)

Table 1

| Sample | Added Amount* | Maximum Density | Fog Density | S10 |
|--------|---------------|-----------------|-------------|-----|
| A      | 2.2           | 1.76            | 0.10        | 42  |
| B      | 0             | 1.76            | 0.12        | 100 |
| C      | 2.2           | 1.62            | 0.29        | 29  |
| D      | 2.2           | 1.86            | 0.20        | 38  |
| E      | 2.2           | 1.70            | 0.16        | 32  |
| F      | 1.1           | 1.74            | 0.13        | 65  |
| G      | 4.4           | 1.68            | 0.15        | 33  |

\*added amount (g) of illustration compound in 1 m<sup>2</sup> [not clearly legible] of sample.

Results in Table 1 show that compared with comparative sample (B), samples of the present invention have a high X-ray sensitivity. Sample (F) with a low content of Illustration Compound (8) shows a low X-ray sensitivity as compared with other examples of the present invention.

## APPLICATION EXAMPLE 2

The samples A and B and sample B' obtained by adhering the sample B to fluorescent sensitization paper (product of Kasei Optonix Co., tradename: Fuji Gurenex G-3) were used for making metal grid X-ray transmission images with variations of the metal grid mesh size; from the images obtained, resolution was estimated from the minimum recognizable mesh. Results are given in Table 2. The resolution is given by the number of recognizable lines in 1 mm.



Table 2

| Sample | Resolution |
|--------|------------|
| A      | 18         |
| B      | 20         |
| B'     | 6          |

Results in Table 2 show that compared with the sample B adhered to the fluorescence sensitization paper, the resolution of sample A and B is superior. As shown in Application Example 1, sample B is inferior in X-ray sensitivity to sample A.

### APPLICATION EXAMPLE 3

Sample H was prepared by installing an underlayer, as described below, to the sample B of Application Example 1.

A dispersion was prepared by dispersing 20 g of Illustration Compound (8) in a mixture of 100 mL of toluene and 100 mL of methyl ethyl ketone, treated with 20 g of polymethyl methacrylate (product of Mitsubishi Rayon Co., tradename: Dianal BR-85), and stirred for dissolution to obtain an underlayer solution, which was then coated using a roll coater to 10 g/m<sup>2</sup> dry to form an underlayer on a photographic base paper.

Sample (I) was prepared using 20 g of Illustration Compound (1) in place of Illustration Compound (8) of sample (H). Sample (J) was obtained similarly as in sample (A), except that an underlayer of sample (H) was installed in the sample (A) of Application Example 1. Sample (K) was obtained similarly as in sample (A), except that an underlayer of sample (I) was installed in the sample (A) of Application Example 1.

The samples thus obtained were subjected to X-ray irradiation and thermal development similarly as in Application Example 1. Results are given in Table 3. For comparison, the results obtained for sample B of Application Example 1 are also shown.

Table 3

| Sample | Added Amount         |            | Maximum Density | Fog Density | S10 |
|--------|----------------------|------------|-----------------|-------------|-----|
|        | Photosensitive Layer | Underlayer |                 |             |     |
| B      | 0                    | 0          | 1.76            | 0.12        | 100 |
| H      | 0                    | 5.0        | 1.77            | 0.12        | 54  |
| I      | 0                    | 5.0        | 1.68            | 0.11        | 33  |
| J      | 2.2                  | 5.0        | 1.74            | 0.14        | 32  |
| K      | 2.2                  | 5.0        | 1.71            | 0.16        | 25  |

\*added amount (g) of illustration compound in 1 m<sup>2</sup> [not clearly legible] of sample.

Results in Table 3 show that compared with comparative sample B, samples of the present invention have high X-ray sensitivity.

## EFFECTS OF THE INVENTION

As clearly shown in the above description, with the thermally developable photosensitive materials, X-ray photographic photosensitive materials having high resolution and high maximum density can be obtained by dry processing.